Waterbody Number WA-CR-1010

SCREENING SURVEY FOR CHEMICAL CONTAMINANTS AND TOXICITY IN SEDIMENTS AT FIVE LOWER COLUMBIA RIVER PORTS SEPTEMBER 22-24, 1987

Art Johnson
Dale Norton

Washington State Department of Ecology Environmental Investigations and Laboratory Services Program Toxics Investigations/Ground Water Monitoring Section Olympia, Washington 98504-6811

December 1988

ABSTRACT

EPA priority pollutants/hazardous substances list compounds and resin acids were analyzed in 12 sediment samples collected at five lower Columbia River ports and an upstream reference area during September 22-24, 1987. Potential for sediment toxicity was assessed through bioassay with two crustacean species, *Hyalella azteca* (amphipod) and *Daphnia pulex* (cladoceran). Ports included in the survey were Camas, Vancouver, Kalama, Longview, and Ilwaco.

Results suggest the level of chemical contamination to be generally low. The sediments were not toxic in bioassay. Additional sampling is recommended to confirm the high concentration and evaluate the extent of polyaromatic hydrocarbons in sediments below the Reynolds aluminum smelter at Longview and possible elevated polychlorinated biphenyls below Reynolds and the VANALCO smelter in Vancouver.

INTRODUCTION

At the request of the Ecology Southwest Regional Office (SWRO), the Toxics Investigations/Ground Water Monitoring Section conducted a reconnaissance survey of sediment quality at five ports along the lower Columbia River during September 22-24, 1987. Survey objectives were to characterize the occurrence of toxic chemicals in the sediments and assess the potential for sediment toxicity. Based on discussions with Gary Bailey and Mike Morhous of SWRO and George Houck of the Ecology Industrial Section, the ports listed below in Table 1 were selected for sampling:

Table 1. Lower Columbia River ports selected for sediment sampling, September 22-24, 1987.

Location	
(approximate river mile)	Potential Sources
Reed Island (124)	reference station
Camas Slough (118)	pulp mill, urban runoff
Vancouver (105-102)	paper mill, aluminum smelter, chemical storage, STP, urban runoff
Kalama (75)	chemical manufacturer
Longview (67-56)	pulp mills, aluminum smelter, former Hg-cell chloralkali plant, log yards, light industry, STP, urban runoff
Ilwaco (3)	boatyards, fishing fleet

METHODS

<u>Sampling</u>--Four stations were sampled at Longview (including Coal Creek Slough), two at Vancouver, and one each at the remaining ports (see Figures 1 and 2). Sediments were collected with a 0.1 m2 van Veen sampler. An effort was made to locate deposits of fine grained sediments. Although several sampling sites are described as being below major industries, no samples were collected in the immediate vicinity of outfalls.

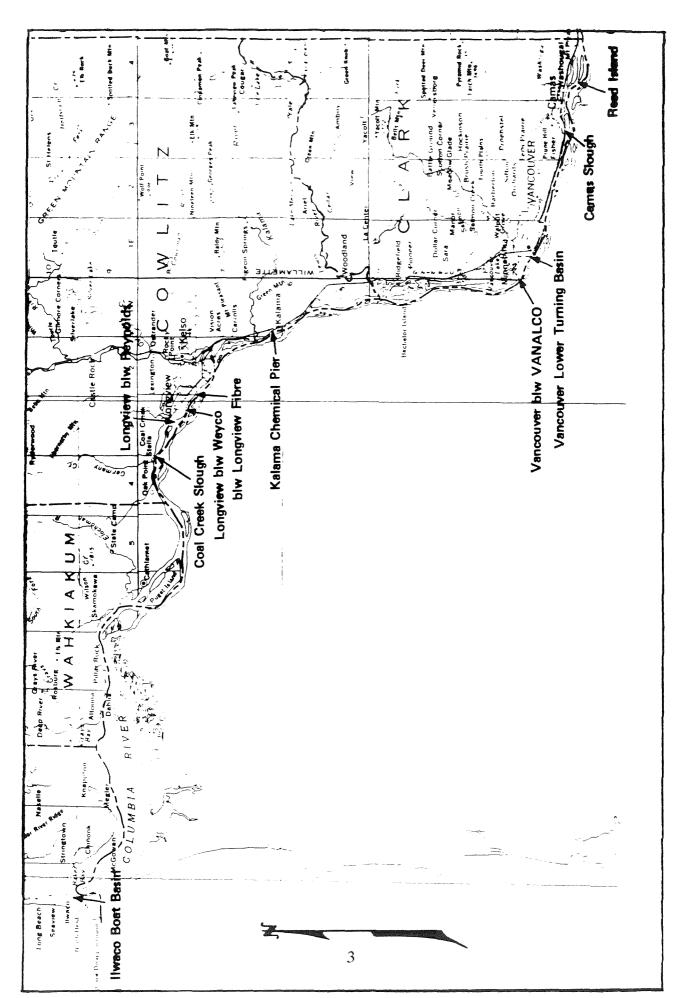
Two to three grabs were pooled for each station. Replicate samples were collected at Camas Slough and at Longview below the Weyerhaeuser pulp mill. The top 2 cm layer from the grabs was pooled and homogenized by stirring with stainless steel spoons in stainless steel beakers, and split into subsamples for analysis. Samples for volatiles analysis were collected by filling 40 mL glass vials (no head space) prior to homogenizing.

Sample handling equipment was cleaned with hot tap water, Liqui-Nox detergent, and sequential rinses of deionized water, dilute nitric acid, deionized water, and pesticide-grade acetone. Sample containers for chemical analyses and bioassays were priority pollutant-cleaned glass jars with teflon-lined lids (I-Chem, Hayward, CA). All samples were stored on ice for transport to the Ecology/EPA Manchester Environmental Laboratory.

Analysis--Table 2 shows the physical/chemical analyses and bioassays done on the sediments. All samples were analyzed for acid/base/neutral compounds and pesticides/PCBs classed as EPA priority pollutants or hazardous substances list (HSL) compounds, grain size, total organic carbon (TOC), and percent moisture. Selected samples were analyzed for priority pollutant/HSL volatiles, cyanide, and resin acids. Appendix A gives a complete list of target chemicals.

The EPA Environmental Research Laboratory in Corvallis, Oregon, conducted bioassays on subsamples from each station. Two acute bioassays were employed: 96-hour exposure of the amphipod *Hyalella azteca* and 48-hour exposure of the cladoceran (water flea) *Daphnia pulex*. Two 1000-mL beakers containing 200 mL sediment and 800 mL of well water were prepared for each sample. Fifteen *Hyalella* were put in each beaker on September 29, 1987; 20 *Daphnia* were placed in the same beakers on October 1, 1987. All animals were counted, and survival recorded on October 3, 1987. The water temperature was 20°C; well water hardness was 20 mg/L. The water was gently aerated during testing (Nebeker, 1987).

Quality assurance for chemical analyses followed standard Manchester laboratory practice (including method blanks, matrix spike duplicates, and surrogate compound spikes) as described in Huntamer (1986). Holding times and spike recoveries were within EPA Contract Laboratory Program (CLP) limits for priority pollutant analysis except for volatiles which exceeded the 14-day holding time for analysis by seven days. The analyses for antimony and neoabietic acid (a resin acid) were of questionable accuracy as described later in this report. Chemical concentrations are reported in units of ug/g (parts per million) or ng/g (parts per billion) on a dry weight basis.



Lower Columbia River sampling sites, September 22-24, 1987 Figure 1.

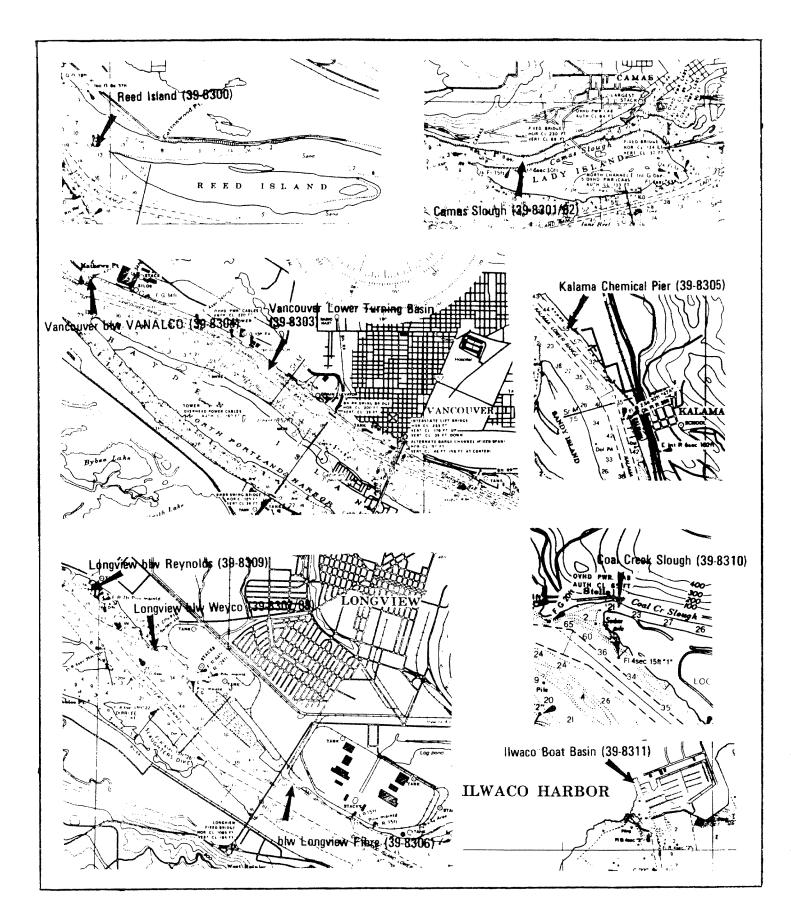


Figure 2. Locations of sediment samples collected at lower Columbia River ports, September 22-24, 1987

Analytical methods for survey of sediment quality at lower Columbia River ports, September 22-24, 1987. Table 2.

Analysis	Method	Reference	Laboratory
Ag, Al, As, Be, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sb, Sn, Tl, Zn	atomic adsorption spectroscopy	EPA (1979)	Laucks Testing Labs, Inc. Seattle, WA
volatiles	<pre>purge and trap/gas chromatography/mass spectroscopy, method 624</pre>	EPA (1984)	Ecology/EPA Environmental Lab, Manchester, WA
acid/base/neutrals	gas chromatography/mass spectroscopy, method 625	EPA (1984)	Ecology/EPA Environmental Lab, Manchester, WA
organochlorine pesticides/ PCBs	<pre>gas chromatography/ electron capture, method 608</pre>	EPA (1984)	Ecology/EPA Environmental Lab, Manchester, WA
cyanide	colorimetric automated UV method 335.3	EPA (1979)	Ecology/EPA Environmental Lab, Manchester, WA
resin acids	<pre>gas chromatography/mass spectroscopy</pre>	NCASI (1986)	Ecology/EPA Environmental Lab, Manchester, WA
grain size	seives and pipettes	Holme & McIntyre (1971)	Parametrix, Inc. Bellevue, WA
total organic carbon	persulfate-UV, method 505	APHA (1985)	Laucks Testing Labs, Inc. Seattle, WA
<u>Hyalella</u> bioassay	96-hour exposure	Nebeker <u>et al</u> . (1986)	EPA Environmental Research Laboratory, Corvallis, OR
<u>Daphnia</u> bioassay	48-hour exposure	EPA (1985) – modified	EPA Environmental Research Laboratory, Corvallis, OR

RESULTS AND DISCUSSION

<u>Physical Characteristics (Table 3)</u>--Sandy sediments with low organic content were typical of most sampling sites. Only the Ilwaco boat basin and Camas Slough sediments were predominantly fine (<62 um) material. These two sites, and perhaps Coal Creek Slough, appeared to be the only depositional environments encountered in the survey.

Metals (Table 3)--Metals concentrations were generally low. Antimony¹, selenium, silver, and thallium were not detectable. Concentrations of other metals were not appreciably elevated above those measured at Reed Island--considered a reference station for purposes of the present study--except for the following:

- Arsenic (9.1 ug/g), beryllium (0.8 ug/g), chromium (26 ug/g), copper (75 ug/g), mercury (0.18 ug/g), and zinc (140 ug/g) in sediments from the Ilwaco boat basin were from 4 to 12 times higher than at Reed Island. The boat basin had the highest concentrations of these five metals, as well as nickel (15 ug/g) and tin (21 ug/g), found in the survey.
- Beryllium and nickel concentrations in Camas Slough were equivalent to those at Ilwaco. Mercury concentrations (0.09 0.10 ug/g) were also moderately elevated compared to other sampling sites.
- The highest lead (140 ug/g) and second highest copper (54 ug/g) concentration--9 and 14 times reference levels, respectively--- occurred at the Vancouver lower turning basin.

Table 4 compares the metals concentrations measured at lower Columbia River ports with levels characteristic of the lower Columbia River drainage and other nearby estuaries. Also shown are interim criteria developed by the Wisconsin Department of Natural Resources (1985) for open-water disposal of sediments dredged from the Great Lakes. These criteria (which are limited to metals) are based on comparisons of current and historical concentrations of contaminants in Great Lakes sediments. Sediment criteria have not yet been established for Washington State freshwaters.

This comparison indicates that even the highest concentrations of arsenic, cadmium, chromium, and nickel observed in the present survey are not appreciably above background, including deep vibracore samples collected in the Columbia River by the U.S. Army Corps of Engineers (COE). Although most sampling sites also had relatively low copper, lead, mercury, and zinc concentrations, lead in the Vancouver lower turning basin, and mercury and zinc at the Ilwaco boat basin exceeded Great Lakes interim dredge disposal criteria. Copper

Quality assurance samples analyzed at the Manchester Laboratory during the time the lower Columbia River samples from the present survey were being processed suggest the antimony data are suspect. Manchester measured only 0.5-0.8 ug/g in duplicate analyses of a NBS standard reference material (River Sediment 1645) containing 51 ug/g. These data have been reported in Johnson (1988).

Table 3. Metals analysis of sediments collected at lower Columbia River ports, September 1987 (µg/g, dry; ppm)

Location:				Vanc. Lower	Vancouver	Kalama				Longview		Ilwaco
	Reed			Turning	below	Chemical			ngview	below		Boat
	Island	-Camas	s Slough-	Basin	VANALCO	Pier				Reynolds		Basin
Depth (ft.):	7	36	36	847	30	36				25		80
Date:	4/22	4/22	4/22	4/22	4/22	4/22				4/23		4/54
Time:	1040	1130	1150	1410	1440	1700				1050		1000
Sample No.(88-398-):	300	301	302	303	304	305	306	307	308	309	310	311
k Fines ^a	0.47	64.29	72.46	7.56			2.77	16.66	19.99	8.28		94.91
k TOC	0.3	1.6	2.8	0.7			0.1	0.2	0.2	0.2		1.6
% Moisture	56.9	52.3	6.43	27.5			76.6	31.0	29.4	28.3		61.8
Antimony*	(<2.5)	(<2.5)	Ī	<u> </u>	(<2.5)	(<2.5)	(<2.5)	(<2.5)	(<2.5)	(<2.5)	(<2.5)	(<2.5)
Arsenic*	2.1	7.2		_			8.0	1.1	1.0	1.1		9.1
Beryllium*	0.1	8-0	0.8				<0.1	<0.1	<0.1	<0.1		0.8
Cadmium*	<0.5	6.0					<0.5	<0.5	<0.5	<0.5		9.0
Tin	9	17	15	12			6	80	10	12		21
Chromium*	12	22	22				œ	7	&	11		56
Copper*	9	31	30				14	16	17	19		75
Lead*	<10	8	22				<10	<10	<10	<10		21
Mercury*	<0.02	0.0	0.10	0.03			<0.02	<0.02	0.02	60.0		0.18
Nickel	6	1.5	15				7	'n	7	6		15
Selenium*	<0.5	<0.5	<0.5				<0.5	<0.5	<0.5	<0.5		<0.5
Silver*	9.0>	9.0>	9.0>				9.0>	9.0>	9.0>	9.0>		9.0>
Thallium*	<0.5	<0.5	<0.5				<0.5	<0.5	<0.5	<0.5		<0.5
Zinc*	9	130	130				1.7	78	31	39		140
Manganese							110	130	130	170		200
Aluminum	7,800 2	23,000	23,000	10,000			5,500	7,000	009,9	006,9		28,000
Iron							1,000	3,000	16,000	000.61		28.000

asilt and clay (<4µm-62µm)
*EPA priority pollutant
() accuracy suspect; see text
+possible anomalous value; see text</pre>

Table 4. Concentrations of selected metals measured in sediments at lower Columbia River ports compared to results of other studies and criteria for disposal of dredged material ($\mu g/g$, dry; ppm)

	Lower Columbia (present		Lower Columbia	Average Columbia	Freshwater
	80th Percentile ^a	Maximum Concentration	River Background Concentrations	River and Oregon Estuaries	Sediment Criteria
Arsenic	3.8	9.1	9.7 <u>+</u> 2.6	6.6 <u>+</u> 0.7	10
Cadmium	<0.5	0.9	0.2 <u>+</u> 0.04	0.4+0.1	1.0
Chromium	16	26	16 <u>+</u> 6.3	29 <u>+</u> 5.8	100
Copper	31	75	16 <u>+</u> 6.4	24 <u>+</u> 3.4	100
Lead	21	140	12 <u>+</u> 1.4	14 <u>+</u> 1.4	50
Mercury	0.09	0.18	0.014+0.006	0.05 <u>+</u> 0.01	0.10
Nickel	11	15	${\tt NA}^{f e}$	29 <u>+</u> 5.5	100
Zinc	95	140	63 <u>+</u> 10	84 <u>+</u> 10	100

 $^{^{\}mathrm{a}}$ eighty percent of stations (i.e., 8 out of 10) had equal to or less than this concentration.

^b U.S. Army Corps of Engineers deep vibracore samples (Festul, 1987).

c average of 150 samples in U.S. Army Corps of Engineers, Portland, database as reported in Festul (1987).

d interim criteria for open water disposal of dredged materials in the Great Lakes; cannot exceed 125 percent of criteria value (Wisconsin Department of Natural Resources, 1985).

e not analyzed.

concentrations at the Illwaco boat basin and Vancouver lower turning basin are above background but within the dredge disposal criteria.

In response to an Ecology compliance order, the Port of Vancouver recently conducted an investigation of impacts from copper concentrate ore spills at the loading facility bordering the lower turning basin (Century West Engineering Corp., 1988). They reported high concentrations of copper (to 54,200 ug/g) and, to a lesser extent, lead (to 796 ug/g), arsenic (to 365 ug/g), zinc (to 5,395 ug/g), and mercury (to 0.25 ug/g) in the immediate vicinity of the loading facility. Downstream of this site only copper concentrations appeared elevated compared to the background levels reported in the document.

Table 5 compares the Port's lower turning basin data (excluding samples at the loading facility) and background data with results from the present survey and previously cited COE data on metals in Columbia River background sediments. Except for lead, Port and Ecology data are in close agreement on metals concentrations in the turning basin. The lead concentration of 140 ug/g reported in the single sample analyzed for Ecology's survey may be an anomaly. The Port's analysis of lead in background sediments agrees well with both Ecology and COE results. Matrix spike recoveries for lead reported in the Port's study also suggest their analyses were accurate.

Except for arsenic and zinc, the Port's data on background concentrations are in line with present study and COE findings. The Port's arsenic data (< 0.05 ug/g in all samples) are suspect. The zinc concentrations reported (134 + /-33 ug/g) may reflect local background, the Port's samples having been collected not far upstream of the turning basin.

The data sources referenced in Table 4 did not include beryllium or tin. Beryllium has been detected in Puget Sound sediments at 0.16 - 1.1 ug/g; average levels in the earth's crust are 6 ug/g (Konasewich et al., 1982). On this basis, sediments at these lower Columbia ports (<0.1 - 0.8 ug/g) do not contain elevated concentrations of beryllium. Although the tin concentration at the Ilwaco boat basin (21 ug/g) was not much above the range at other ports (8-17 ug/g), the amount of organo-tin present would be the critical factor in determining its significance. Organo-tins were not analyzed for the present survey.

<u>Volatiles</u>--This analysis was limited to sites with potential pulp mill influence--Camas Slough, the Vancouver lower turning basin, Longview below Weyerhaeuser--and the Reed Island reference station. No compounds were detected at detection limits ranging from 1.4 to 15 ng/g. As already noted, the 14-day holding time for analysis was exceeded by one week for these samples.

Analysis for volatiles in sediments off the Kalama Chemical pier was recently done as part of an Ecology Class II inspection (Heffner, 1988). Only trace amounts (less than 1 ng/g) of two compounds, toluene and 1,1,1-trichloroethane, were detected near the pier. 1,1,1-Trichloroethane, however, was also detected (4.4 ng/g) upstream of the pier.

Acid/Base/Neutrals (Table 6)--Polyaromatic hydrocarbons (PAH) and phthalate acid esters (PAE) were detected at all sites. Dibenzofuran, an oxygen-containing 2-ring aromatic

Table 5. Comparison of metals concentrations measured by the Port of Vancouver, Ecology, and COE in sediments from the Vancouver lower turning basin and/or background sediments (ug/g, dry; ppm).

	Vancouver Lower T	Curning Basin	Lower Colu	mbia Rive	r Background
		Ecology		Ecology	
	Port Data ^a	Data ^b	Port Data ^c	Datad	COE Data ^e
Arsenic	2.7 <u>+</u> 1.2	3.8	<0.05 ± 0	2.1	9.7 ± 2.6
Cadmium	NAf	<0.5	NA	<0.5	0.2 ± 0.04
Chromium	6.8 <u>+</u> 4.0	13	8.0 ± 1.6	12	16 ± 6.3
Copper	49 <u>+</u> 44	54	23.0 ± 5.5	6	16 <u>+</u> 6.4
Lead	7.4 ± 7.6	140	16.7 ± 6.2	<10	12 <u>+</u> 1.4
Mercury	0.035 ± 0.016	0.03	0.07 ± 0.03	<0.02	0.014 ± 0.006
Nickel	NA	11	NA	9	NA
Zinc	97 <u>+</u> 62	95	134 <u>+</u> 33	40	63 <u>+</u> 10

 $^{^{\}rm a}$ mean \pm SD of 32 samples (Century West Engineering Corp., 1988)

b sample no. 85-398303, present survey

 $^{^{\}rm c}$ mean \pm SD of 5 samples (Century West Engineering Corp., 1988)

d sample no. 88-398300 (Reed Island), present survey

edeep vibracore samples (Festul, 1987)

f not analyzed

Organic priority pollutants/hazardous substances list compounds detected in the acid-base/neutrals fraction of sediments collected at lower Columbia River ports, September 1987 ng/g dry) Table 6.

Location:				Vanc. Lower	Vancouver	Kalama	Below			Longview	Coal	Ilwaco
	Reed			Turning	below	Chemical	Longview	Longview	ем	below	Creek	Boat
	Island	-Camas	Camas Slough-	Basin	Ϋ́	Pier	Fibre	below Weyco-	eyco	Reynolds	Slough	Basin
Depth (ft.):	7	36	_36	87		36	67	19	18	25	$2\overline{1}$	œ
Date:	4/22	4/22	4/22	4/22		4/22	4/23	4/23	4/23	4/23	4/23	4/24
Time:	1040	1130	1150	1410		1700	1000	1020	1035	1050	1125	1000
Sample No. (88-398-):	300	301	302	303	304	305	306	307	308	309	310	311
9 D: a	74.0	64. 30	77 46	7 56	11 02	1 27	77 6	16.66	10 00	8 28	25 4.2	0 01
A FINES	÷ .	67.50	7.	2.0	77.77	7.7		70.0	10.00	3.0	4.0	1 6
7 JOC	0.3	0 · 1	7.8	/ 0	6.0	7.0	1.0	7.0	7.0	7.0	· · ·	1.0
% Moisture	26.9	52.3	54.9	27.5	30.3	28.7	26.6	31.0	29.4	28.3	34.8	61.8
Polyaromatic Hydrocarbons (PAH):	PAH):											
naphthalene	120u	190u	840u	22J	P.	1103	130u	140u		530u		44.3
2-methylnapthalene	120u	37	14.3	6 3	4.3	1.1	4.3	33		6.3		17.1
acenaphthylene	120u	190u	840u	4.3	2.3	110u	130u	140u	130u	530u	140u	123
acenaphthene	120u	190u	840n	5.7	93	110u	24.3	6.3		94.3		14.3
fluorene	120u	1.1	93	93	9.1	110u	15J	7.3		49.1		34.3
phenanthrene	11	8.	59.1	653	71.5	33	42.3	41.1		580		1803
anthracene	120u	190u	840n	12J	6.7	110u	53	6.7		460J		1,500u
fluoranthene	0.53	8.1	72.5	1603	196	4.3	403	681		2,100		1,500u
pyrene	120u	93	807	160J	787	5.1	50.1	1303		2,500		290J
benzo(a)anthracene	120u	6.3	50J	623	45J	5.1	21.3	£99		2,200		1807
chrysene	120u	13	58.1	653	663	5.1	15J	733		4,100		2007
benzo(b)fluoranthene	2BJ	6BJ	32BJ	26BJ	31BJ	110BJ	10BJ	41BJ		1,800B		99BJ
benzo(k)fluoranthene	2BJ	190BJ	26BJ	20BJ	22BJ	3BJ	8BJ	31BJ		910B		120BJ
benzo(a)pyrene	120Bu	190Bu	840Bu	33BJ	47BJ	110Bu	13BJ	66BJ		1,500B		1,500u
indeno(1,2,3-cd)pyrene	120u	190u	840n	17.1	33J	110u	10)	423		920		763
dibenzo(a,h)anthracene	120Bu	190Bu	840Bu	520Bu	12BJ	110Bu	78.7	25BJ		400BJ		1,500Bu
benzo(g,h,i)perylene	120Bu	190Bu	37BJ	22BJ	39BJ	110Bu	8BJ	51BJ		1,100B		1,500Bu
Total PAH detected:	Q	84	440	069	580	70	270	069	400 1	000,61	220	1,600
		1								•		•
Other Aromatic Hydrocarbons dibenzofuran	;; 120u	190u	840n	7.3	7.3	110u	113	5.3	<u>19</u>	28J	33	28J

a silt + clay (<4μm-62μm)
u = not detected at detection limit shown
J = estimated concentration
B = also detected in laboratory blank (see text)</pre>

Table 6. (continued)

Location:	-			Vanc. Lower	Vancouver	Kalama	Below	,		Longview	Coal	Ilwaco
	Keed			Turning	pelow	Chemical	Longview	Long	Longview	pelow	Creek	Boat
	Island	-Camas	-Camas Slough-	Basin	VANALCO	Pier	Fibre	below	-below Weyco	Reynolds	Slough	Basin
Depth (ft.):	7	36	36	84	30	36	67	19	18	25	21	∞
Date:	4/22	4/22	4/22	4/22	4/22	4/22	4/23	4/23	4/23	4/23	4/23	4/24
Time:	1040	1130	1150	1410	1440	1700	1000	1020	1035	1050	1125	1000
Sample No. (88-398-):	300	301	302	303	304	305	306	307	308	309	310	311
% Fines	0.47	64.29	72.46	7.56	11.02	1.27	2.17	16.66	19.99	8.28	25.42	94.91
Z TOC	0.3	1.6	2.8	0.7	0.3	0.2	0.1	0.2	0.2	0.2	0.3	1.6
% Moisture	26.9	52.3	54.9	27.5	30.3	28.7	26.6	31.0	29.4	28.3	34.8	61.8
Phthalate Acid Esters (PAE):												
diethylphthalate	33	190u	4.3	2.3	2.1	110u	130u	2.3	130u	530 u	140u	1,500u
di-n-butvlohthalate	25.3	16	8407	41J	650u	15J	123	32J	19.1	530u		1,500u
butylbenzylphthalate	2.3	190u	840u	260u	130u	1.1	130u	140u	101	530u		1,500u
bis(2-ethylhexyl)-	64BJ	16BJ	170BJ	338J	2108	1,900B	20J	27BJ	44BJ	47BJ	62BJ	570BJ
phthalate	1 07	1691	1367	1 000	1 00	187	1 7	1 40	1481	5308	6381	64B.1
di-n-octyiphthalate	2	1000	/4PA	7007	200	3	?	3	7	nanco	200	2
Total PAE detected:	100	41	1,100	96	220	1,900	36	70	87	47	140	630
Miscellaneous Compounds: isophorone	120u	190u	8404	260u	74	110u	130u	140ո	130u	530u	140u	1,500u
Tentative Identifications:												
2,4,5,7-tetramethyl-	Ð	F006	2,4003	4,2003	S.	Q	QN	ND	6,2003	QN	N	GN.
pnenantnrene benzo(i)fluoranthene	S	ON	QN	QN QN	Ð	ND	CIN	QN	ND 1	2,0003	QN	QN
benzo(b)triphenylene	QN	QN.	Q	QN	ND	QN	e e	NO	QN	3,100J	QN	ND
benzo(b)naphtho-	Q	Ê	CIN	ND	QN	ND	ON.	Q		6,100J	Q	Q.
(1,2-d)thiophene	į	g	Ę	1 000	1001	GIN.	CI.	CIN	CIN	CIN.	NID	Ę
2,2-diethyl-1,1-biphenyl	S E	ON 1	ND 1	2068 UN	7807 E	3 5	Q (N	2 E	710.1	€ €	1 000	Z S
d-ifiedoolean-14-en-one	O. I	7,000 t	7,700	Q.	Q.	3		9	0010	2	2000 1	

a silt + clay (<4µm-62µm)

u = not detected at detection limit shown

J = estimated concentration

B = also detected in laboratory blank (see text)

ND = not detected

hydrocarbon was also detected at most sites except Reed Island, Camas Slough, and the Kalama Chemical pier. A trace (estimated at 4 ng/g) of isophorone (trimethylcyclohexenone), a solvent and intermediate in chemical synthesis, was detected at Vancouver below the VANALCO aluminum smelter.

In most cases concentrations of the above compounds were below detection limits and reported by the laboratory as estimates. One of the two method blanks analyzed in conjunction with these samples also had detectable amounts of five high molecular weight PAH (3-8 ng/g) and two PAE (5-10 ng/g). The data are so qualified in the table.

The primary result of interest in this analysis is the elevated concentrations of high molecular weight PAH (400-4,100 ng/g individual PAH; 19,000 ng/g total detected PAH) in the sediments collected at Longview below the Reynolds aluminum smelter. These concentrations are one to three orders of magnitude higher than found at the other ports and exceed some of the apparent effects thresholds (AET²) that have been determined for PAH in Puget Sound sediments (PTI Environmental Services, 1988). Similar concentrations of aromatic hydrocarbons not classed as EPA priority pollutants were also tentatively identified below Reynolds (and at several other sites).

According to Ted Mix and Dave Davies of the Ecology Industrial Section, PAH are released when anodes are consumed in the aluminum smelting process. PAH (monitored by way of benzo(a)pyrene) are among the constituents currently limited in Reynolds' NPDES permit. The extent of PAH contamination at this facility or its potential as a PAH source to the river has not been investigated. The Industrial Section has begun discussions with the aluminum industries and EPA on control of PAH released through air emissions, and will be requiring complete priority pollutant scans on effluents and stormwater discharges when Reynolds' NPDES permit comes up for renewal next year (Davies, personal communication).

The total PAH concentration at the Ilwaco boat basin (1,600 ng/g), although much lower than at Longview below Reynolds, was 2 to 6 times higher than at the other ports. PAH concentrations at Ilwaco do not, however, approach even the lowest of Puget Sound AET values for individual PAH (230 ng/g).

<u>Chlorinated Pesticides</u>—With one exception, pesticides were not detected in the Columbia ports sediments. The limit of detection was 2.0 ng/g (60 ng/g for toxaphene). These results are consistent with data reported by USGS for the lower Columbia River and nearby drainages which show organochlorines to be generally at or below limits of detection in the sediments

An AET is the sediment concentration of a chemical above which a statistically significant biological effect (relative to reference sediments) is always observed. The biological indicators used include depressions in benthic infauna and results of amphipod (Rhepoxynius abronius), oyster larvae (Crassostrea gigas), and Microtox bioassays. The AET values cited in the present report are based on data from up to 284 stations in Puget Sound.

(Fuhrer, 1984: Fuhrer and Rinella, 1982). The Manchester laboratory reported 141 ng/g of endosulfan sulfate in sediments from Longview below Reynolds but encountered interferences in the analysis of this compound and qualified the result "presumptive evidence for presence of material."

<u>Polychlorinated Biphenyls</u>--PCBs (quantified as Aroclor-1254) were detected at two locations only--Longview below Reynolds (73 ng/g) and Vancouver below VANALCO (58 ng/g). Detection limits for other sites were 20 ng/g.

Neff <u>et al.</u> (1986) have proposed a freshwater sediment criterion of 290 ug/g (TOC normalized) for PCBs. This value, derived from field data, is the highest sediment concentration tolerated by 95 percent of benthic infauna. Although PCB concentrations of 58 and 73 ng/g (19 and 36 ug/g, respectively, when normalized to TOC) are within Neff's criterion and below Puget Sound AET values (130 - 3,100 ng/g), results of the present study and the above-referenced USGS analyses of Columbia River sediments suggest the concentrations measured below Reynolds and VANALCO are relatively high for the lower Columbia and may, therefore, indicate past or present sources.

One small discharge of PCBs is known to have occurred at VANALCO. According to Dave Davies, a 1982 inspection by the Department of Labor and Industries found evidence of air contamination with PCBs at the VANALCO wire mill (now owned by ACPC, a separate company). The source was traced to a 250,000-gallon tank of oil used to lubricate the wire-rolling machinery.

VANALCO used a filtration system to treat and re-use the oil. However, wastewater resulting from filtration became contaminated with PCBs. Between 1983 and 1984, in consultation with Ecology and EPA, this water was disposed of by bleeding into the plant's NPDES discharge to the Columbia River (5 MGD) at a rate calculated to result in conformance with the EPA health risk level of 10⁻⁵ (0.79 ng/L) after mixing with other process effluents. Ecology records indicate less than 10 grams of PCBs were discharged to the Columbia in this manner.

<u>Cyanide</u>--This analysis was limited to sediments near aluminum smelters and Reed Island. Cyanide was not detected at any of these sites at a detection limit of 5 ng/g.

Resin Acids (Table 7)--Only the three sites with potential pulp mill influence and Reed Island were analyzed for resin acids. The basic structure of the compounds considered here consists of a three-ring aromatic hydrocarbon (phenanthrene) with a carboxyl group (-COOH). Resin acids are naturally occurring compounds but are much concentrated through both chemical and mechanical pulping processes (Keith, 1976; Oikari and Holmbom, 1986). Chlorinated resin acids are unique to bleach mills using chlorine.

Resin acids were detected at each of the sampling sites below pulp mills, but not at Reed Island. A chlorinated resin acid, dichlorodehydroabietic acid, was detected in the Vancouver lower turning basin (60 ng/g, estimated) and at Longview below Weyerhaeuser (42 ng/g, estimated). Total resin acid concentrations were 2,000 ng/g at Camas Slough, 570 ng/g at the Vancouver lower turning basin, and 1,400 ng/g at Longview below Weyerhaeuser. Other sources of data

Resin acids detected in sediments collected at selected lower Columbia River ports, September 1987 (ng/g, dry; ppb)

Location:	Reed Island	Camas Slough	Vancouver Lower	Longview
			Turning Basin	bw Weyco
Depth (ft.):	7	36	48	19
Date:	4/22	4/22	4/22	4/23
Time:	1040	1130	1410	1020
Sample No. (88-398-):	300	301	303	307
% Fines ^a	0.47	64.29	7.56	16.66
% TOC	0.3	1.6	0.7	0.2
% Moisture	26.9	52.3	27.5	31.0
% MOISCULE	20.9	32.3	27.3	31.0
Abietic acid	120 u	5 00	110	300
Neoabietic acid	(120u)	(300u)	(100u)	(130u)
Dehydroabietic acid	120u	920	240	5 00
Dichlorodehydro-	120 u	300u	60J	42J
abietic acid				
Isopimaric acid	120 u	5 00	130	340
Sandaracopimaric acid	120 u	130J	32J	130u
Levopimaric acid	120 u	300u	100 u	130u
Palustric acid	120u	300u	100u	170
Total detected				
resin acids:	ND	2,000	570	1,400

asilt + clay (<4um-62µm) u = not detected at detection limit shown

^{() =} low matrix spike recoveries (1.4%-6.5%) for this compound

J = estimated concentration

ND = not detected

on resin acids in Columbia River sediments were not available to put these findings in perspective, but limited resin acid analyses have been done in Puget Sound. Recent analysis of Port Townsend Bay sediments by the Manchester laboratory suggests individual resin acid concentrations of 2,000 ng/g or more are not unusual in the vicinity of pulp mills (Johnson, 1988). In Everett Harbor's East Waterway, individual resin acid concentrations approach 100,000 ng/g (PTI Environmental Services and Tetra Tech, 1988). The significance of resin acid contamination of aquatic sediments has not been determined.

<u>Bioassays (Table 8)</u>--None of the sediments assayed appeared to have substantial toxicity toward *Hyalella* or *Daphnia*. Little or no mortality occurred among *Hyalella*. Although in most instances *Daphnia* experienced mortality in the range of 5 to 25 percent, the highest mortality--25 to 30 percent---occurred in Reed Island reference sediments. This suggests the *Daphnia* mortality observed for port sediments is probably not significant.

CONCLUSIONS

Results of this limited survey of sediment quality at lower Columbia River ports suggest the level of chemical contamination to be generally low. This may reflect the non-depositional character of most of the sites investigated, rather than the absence of contaminant sources. The sediments did not appear toxic in short-term bioassays with two species of crustaceans.

RECOMMENDATIONS

- Additional Columbia River sediment samples should be collected to confirm the high concentration of PAH at Longview below the Reynolds aluminum smelter, and determine the extent of contamination.
- Sampling to confirm elevated PCBs should also be done at the Reynolds site and at Vancouver below the VANALCO aluminum smelter.
- A few sediment samples from the Reynolds site should be analyzed for endosulfan sulfate to determine whether the tentative presence of this compound can be confirmed.
- Copper, mercury, zinc, and PAH appeared somewhat elevated at the Ilwaco boat basin but the value of focusing on this particular finding is questionable considering the widespread use of copper--and (historically) mercury--containing anti-fouling paints, sacrificial zinc anodes, gasoline, and diesel fuel at these types of facilities. Mercury is no longer registered for use in anti-fouling paints (EPA, 1980).

Table 8. Bioassay results on sediments collected at lower Columbia River ports, September 22-24, 1987 (duplicate samples).

	Sample No.		la (n = 15)		n = 20
Location	(88-398-)	No. Dead	% Mortality	No. Dead	% Mortality
I - h - unt nur nont wol	A	2	13	0	0
Laboratory control	В	0	0	Ö	0
	n	O	Ü	v	ū
Reed Island	300A	1	7	6	30
	300B	1	7	5	25
Camas Slough	301A	2	13	3	15
Camas Stough	301B	0	0	1	5
	302A	0	0	1	5
	302B	0	Ö	1	5
	3025	V	O	.	~
Vancouver Lower	303A	0	0	1	5
Turning Basin	303B	0	0	3	15
Vancouver below	304A	1	7	2	10
VANALCO	304B	0	0	1	5
VANALCO	2040	V	v	-	
Kalama Chemical Pier	305A	1	7	3	15
	305B	1	7	3	15
Below Longview Fibre	306A	0	0	4	20
Delow hongview libre	306B	0	0	5	25
Ii below Waysa	307A	0	0	4	20
Longview below Weyco	307B	1	7 '	0	0
	307B 308A	0	Ô	3	15
	308B	0	0	0	0
	abuc	U	U	O	· ·
Longview below	309A	0	0	4	20
Reynolds	309B	0	0	5	25
Coal Creek Slough	310A	0	0	3	15
Cour or con prought	310B	0	0	2	10
Tlance Book Doo!-	311A	0	0	0	0
Ilwaco Boat Basin	311B	0	0	Ő	Ő
	2110	U	V	O	v

REFERENCES

- American Public Health Association, 1985. Standard methods for the examination of water and wastewater. 16th ed. Washington, D.C. 1,268 pp.
- Century West Engineering Corp., 1988. Report of findings--Columbia River Impact Investigation. Portland, OR. 10pp + tables.
- EPA, 1979. Methods for chemical analysis of water and wastes.
- EPA, 1980. Ambient water quality criteria for mercury-1984. EPA 440/5-84-026. 136 pp.
- EPA, 1984. Guidelines establishing test procedures for the analysis of pollutants under the Clean Water Act: final rule and interim final rule and proposed rule. Federal Register 40 (209): 1-210.
- EPA, 1985. Methods for measuring the acute toxicity of effluents to freshwater and marine organisms. EPA 600/4-85-013.
- Festul, D., 1987. Tiered testing for metals in Oregon sediments. U.S. Army Corps of Engineers. Portland, OR. 33pp.
- Fuhrer, G.J., 1984. Chemical analyses of elutriates, native water, and bottom material from the Chetco, Rogue, and Columbia Rivers in western Oregon, USGS Open-file Report 84-133, 57 pp.
- Fuhrer, G.J. and F.A. Rinella, 1982. Analyses of elutriates, native water, and bottom material in selected rivers and estuaries in western Oregon and Washington. USGS Open-file Report 82-922, 147 pp.
- Heffner, M., 1988 (in prep.). Kalama Chemical Class II Inspection. Wash. St. Dept. of Ecology, Olympia, WA.
- Holme, N.A. and A.D. McIntyre, 1971. Methods for the study of marine benthos. IBP Handbook No. 16.
- Huntamer, D., 1986. Department of Ecology, Laboratory User's Manual. Manchester Environmental Laboratory, Manchester, WA.
- Johnson, A., 1988. Port Townsend pen-reared salmon mortality: results of screening surveys for toxic chemicals in tissues, sediments, seawater and effluents, October-December 1987. Wash. St. Dept. of Ecology, Olympia, WA. 33 pp.
- Keith, L.H., 1976. Identification of organic compounds in unbleached treated Kraft pulp mill wastes. Environ. Sci. Technol. 10(6):555-564.

- Konasewich, D.E., P.M. Chapman, E. Gerencher, G. Vigers and N. Treolar, 1982. Effects, pathways, processes, and transformation of Puget Sound contaminants of concern. NOAA Tech. Memo. OMPA-20. 357 pp.
- National Council for Air and Stream Improvement, 1986. Procedures for the analysis of resin and fatty acids in pulp mill effluents. Tech. Bull. 501. New York, N.Y.
- Nebeker, A.V., M.A. Cairns, J.H. Gakstatter, K.W. Malueg, G.S. Schuytema and D.F. Krawgzyk, 1986. Biological methods for determining toxicity of contaminated sediments to invertebrates. Environ. Toxicol. Chem. 3:617-630.
- Nebeker, A.V., 1987. EPA Environmental Research Laboratory, Corvallis, OR. Letter to A. Johnson, Wash. St. Dept. of Ecology.
- Neff, J.M., D.I. Bean, B.W. Cornaby, R.M. Vaga, T.C. Gulbraunsen, and J.A. Scanlon, 1986. Sediment quality criteria methodology validation: calculation of screening level concentrations from field data. Battelle, Washington, D.C.
- Oikari A. and B. Holmbom, 1986. Assessment of water contamination by chlorophenolics and resin acid with the aid of fish bile metabolites. pp. 252-267 in Poston, T.M. and R. Purdy (eds.) Aquatic Toxicology and Environmental Fate: Ninth Volume ASTM STP 921.
- PTI Environmental Services, 1988. Sediment quality values refinement: Tables 3 and 5 1988 update and evaluation of Puget Sound AET. <u>for USEPA Region X</u>, Office of Puget Sound, Seattle, WA.
- PTI Environmental Services and Tetra Tech, Inc.. 1988. Everett Harbor Action Program: Analysis of toxic problem areas. <u>for EPA Region X</u>, Office of Puget Sound, Seattle, WA.
- Wisconsin Department of Natural Resources, 1985. Report of the technical subcommittee on determination of dredge material suitability for in-water disposal. Madison, WI.

Appendix A. Chemicals analyzed in sediments collected at lower Columbia River ports, September 22-24, 1987

Volatiles	Acid/Race/Nontrale		
Chloromethane	Pheno1	Anthracene	Abiotic soid
Bromomethane	bis(2-Chloroethyl)ether	di-n-Butylphthalate	Neoabietic acid
Vinyl chloride	2-Chlorophenol	Fluoranthene	Dehydroabietic acid
Chloroethane	1,3-Dichlorobenzene	Pyrene	Dichlorodehydroabietic acid
Methylene chloride	1,4-Dichlorobenzene	Butylbenzylphthalate	
Acetone	Benzyl alcohol	3,3'-Dichlorobenzidine	Levopimaric acid
Carbon disulfide	1,2-Dichlorobenzene	Benzo(a)anthracene	Sandaraconimaric acid
1,1-Dichloroethene	2-Methylphenol	bis(2-Ethvlhexvl)pthalate	
1,1-Dichloroethane	bis(2-Chloroisopropy1)ether	Chrysene	71000
trans-1,2-Dichloroethene	4-Methylphenol	di-n-Octvlohthalate	
Chloroform	N-Nitroso-di-n-propylamine	Benzo(b)fluoranthene &	Motals
1.2-Dichloroethane	Hexachloroethane		Antimonic
7-Rutanone	Nitrobonsone	Ponzo(a)nimono	AllLimony
1 1 1-Trichlorothans	Tophorono	Tadono(1 2 2 ad) access	Arsenic
Combon totacoblosido	Taoping oile	Indeno(1,2,3-cd)pyrene	Beryllium
carpon recraciior me		Dibenzo(a,n)anthracene	Cadmium
vinyi acetate	Z,4-Dimetnyiphenol	benzo(ghi)peylene	Tin
bromodichloromethane	Benzoic acid		Chromium
1,2-Dichloropropane	bis(2-Chloroethoxy)methane		Copper
trans-1,3-Dichloropropene	2,4-Dichlorophenol		Lead
Trichloroethene	1,2,4-Trichlorobenzene		Mercury
Dibromochloromethane	Naphthalene		Nickel
1,1,2-Trichloroethane	4-Chloroaniline		Selenium
Benzene	Hexachlorobutadiene		Silver
cis-1,3-Dichloropropene	4-Chloro-3-methylphenol	OC Pesticides/PCBs	Thallium
2-Chloroethylvinylether	2-Methylnaphthalene	alpha-BHC	Zinc
Bromoform	Hexachlorocyclopentadiene	beta-BHC	Manganese
4-Methyl-2-pentanone	2.4.6-Trichlorophenol	delta-BHC	Aliminim
2-Hexanone	2,4,5-Trichlorophenol	gamma-BHC (Lindane)	Tron
Tetrachloroethene	2-Chloronaphthalene		***
1.1.2.2-Tetrachloroethane	2-Nitroaniline	Aldrin	
Toluene	Dimethylphthalate	Hentachlor epoxide	
Chlorobenzene	Acenaphthylene		Miconellace Miconellace
Frhylbanzana	3-Nitroaniline	Dieldrin	Created
Styrene	Chaisol	Dieluliii	cyantue
Total Xvlenes	Acenaphthene	ריי לידר החלתיו	
rocar nytenes	7 4-Dinitronhenol	Endosulfan II	
	/-Nitrophonol	n n thun	
	Dibenzofuran	Figure 1 fan en fate	
	2.4-Dinitrotoluene	n.n'-DDT	
	2 6-Dinitrotoluene	Methovichlor	
	Diethylphthalate	Francisco de la constanta de l	
	Lettly ipitting face	Chlordan	
	Plucies	a	
	ruorene	Toxaphene	
	4-Nitroaniline	PCB-1016	
	W.Witnessdieksenglopies	FCB-1242	
	N-Nitrosogiphenylamine(I)	PCB-1248 DCB-1254	
	4-biomophenyi-phenyiemer Hexachlorobenzene	FCD-1234 PCR-1260	
	Pentachlorophenol	0071 001	
	Phenanthrene		
	1 11 California Const		